PATENT ABSTRACTS OF JAPAN

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(71)Applicant: MITSUBISHI GAS CHEM CO INC

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(72)Inventor: MOTOORI SUSUMU

(54) LIQUID CYANIC ACID ESTER RESIN COMPOSITION AND SEMICONDUCTOR SEALING DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a liquid cyanic acid ester resin composition having excellent adhesivity, heat-resistance, moisture resistance, electrical properties, etc., and provide a semiconductor sealing device produced by sealing a semiconductor element with the cured liquid cyanic acid ester resin composition.

SOLUTION: This composition is produced by mixing 100 pts.wt. of a resin composition composed of (A) 25-60 pts.wt. of a cyanic acid ester resin, (B) 35-70 pts.wt. of an epoxy resin exhibiting liquid state at room temperature and (C) 0.1-5 pts.wt. of an epoxy-containing silicone oil preparatorily mixed to the cyanic acid ester resin with (D) 0.1-5 pts.wt. of a curing catalyst consisting of a metal chelate or a metal salt and (E) 100-900 pts.wt. of a filler.

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     130:25998
ED
     Entered STN: 02 Nov 1998
ΤI
     Cyanate ester polymer-containing liquid epoxy
     compositions and semiconductor devices sealed with them
IN
     Motoori, Susumu
     Mitsubishi Gas Chemical Co., Ltd., Japan
PA
     Jpn. Kokai Tokkyo Koho, 5 pp.
SO
     CODEN: JKXXAF
DΤ
     Patent
LΑ
     Japanese
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     ICM C08L079-00
     ICS C08L063-00; C08L083-06; H01L023-29; H01L023-31
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     38-3 (Plastics Fabrication and Uses)
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PRAI JP 1997-96039
                               19970414
CLASS
 PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES
 ______
 JP 10287809 ICM C08L079-00
                ICS
                       C08L063-00; C08L083-06; H01L023-29; H01L023-31
     The compns. comprise (A) cyanate ester polymers 25-60,
     (B) liquid epoxy resin 35-70, (C) epoxy-containing
     silicone oils which are pre-mixed with the cyanate ester
     polymers before use, 0.1-5 parts, (D) 0.1-5 phr (based on A+B+C) metal
     chelate or metal salt-type curing catalysts, and (E) 100-900 phr fillers.
    Thus a composition containing a cyanate ester prepolymer
     (viscosity 0.10 P at 100°) 15, Epiclon 830LVP (a bisphenol F-type
     epoxy resin) 55, neopentyl glycol diglycidyl
     ether 15, and a mixture of 2,2-bis(4-cvanatophenyl)propane and BY 16-855
     (epoxy-terminated di-Me siloxane) 15 was blended with Fe acetylacetone
     1.0, A 187 2, spherical SiO2 400, and MA 100 0.5 part to give a liquid
     composition which was applied on a Si chip, and cured at 160° for 3 h to
     give a test piece showing high glass-transition temperature, good adhesion,
     moisture and solder-heat resistances, and less warpage.
     cyanate ester polymer liq semiconductor
     sealing; bisphenol epoxy resin
     polycyanate electronic packaging; silicone oil epoxy
     polycyanate semiconductor sealant; metal chelate
     catalyst polycyanate epoxy compn; acetoacetate catalyst
     polycyanate epoxy electronic packaging; chelate catalyst
     polycyanate epoxy electronic packaging
ΙT
     Crosslinking catalysts
        (chelating agents; cyanate ester polymer-based liquid
        compns. for sealing semiconductor devices)
IT
     Chelates
     RL: CAT (Catalyst use); USES (Uses)
        (crosslinking catalysts; cyanate ester
       polymer-based liquid compns. for sealing semiconductor devices)
IT
     Electronic packaging materials
        (cyanate ester polymer-containing liquid epoxy compns.
       and semiconductor devices sealed with them)
ΙT
    Butadiene rubber, uses
    RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
    engineered material use); USES (Uses)
        (epoxidized, E-1000-3.5; cyanate ester
       polymer-containing liquid epoxy compns. and semiconductor devices sealed
with
       them)
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Polysiloxanes, uses
IΤ
     Polysiloxanes, uses
     RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
     engineered material use); USES (Uses)
        (epoxy, SF 8411; crosslinked with cyanate ester and
        epoxy resins, liquid compns. for sealing
        semiconductor devices)
ΙT
     Polysiloxanes, uses
     Polysiloxanes, uses
     RL: IMF (Industrial manufacture); POF (Polymer in formulation); PRP
     (Properties); TEM (Technical or engineered material use); PREP
     (Preparation); USES (Uses)
        (epoxy, polycyanate-; cyanate ester
        polymer-containing liquid epoxy compns. and semiconductor devices sealed
with
        them)
ΙT
    Water-resistant materials
     Water-resistant materials
        (heat-resistant; cyanate ester polymer-containing liquid
        epoxy compns. and semiconductor devices sealed with them)
IT
    Epoxy resins, uses
       Epoxy resins, uses
     RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
     engineered material use); USES (Uses)
        (polysiloxane-, SF 8411; crosslinked with cyanate
        ester and epoxy resins, liquid compns. for
        sealing semiconductor devices)
IT
     Epoxy resins, uses
       Epoxy resins, uses
     RL: IMF (Industrial manufacture); POF (Polymer in formulation); PRP
     (Properties); TEM (Technical or engineered material use); PREP
     (Preparation); USES (Uses)
        (polysiloxane-, polycyanate-; cyanate ester
        polymer-containing liquid epoxy compns. and semiconductor devices sealed
with
    Heat-resistant materials
    Heat-resistant materials
        (water-resistant; cyanate ester polymer-containing liquid
        epoxy compns. and semiconductor devices sealed with them)
ΙT
    9003-17-2
    RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
     engineered material use); USES (Uses)
        (butadiene rubber, epoxidized, E-1000-3.5; cyanate
        ester polymer-containing liquid epoxy compns. and semiconductor
        devices sealed with them)
ΙT
     14024-18-1
    RL: CAT (Catalyst use); USES (Uses)
        (catalysts; cyanate ester polymer-containing liquid epoxy
        compns. and semiconductor devices sealed with them)
IT
    1156-51-0DP, 2,2-Bis(4-cyanatophenyl) propane, polymers with
    epoxy-terminated siloxane, E 1000-3.5, and epoxy resins
    17557-23-2DP, Neopentyl glycol diglycidyl ether, polymers with
    biscyanatophenylpropane, E 1000-3.5, Epiclon 830LVP, epoxy-terminated
    siloxane and neopentyl glycol diglycidyl ether 96141-20-7DP,
    Epiclon 830LVP, polymers with biscyanatophenylpropane, E 1000-3.5,
    epoxy-terminated siloxane and neopentyl glycol diglycidyl ether
    190185-64-9DP, polymers with biscyanatophenylpropane, E 1000-3.5, and
    other epoxy resins 216220-24-5P
    216220-25-6P
    RL: IMF (Industrial manufacture); POF (Polymer in formulation); PRP
     (Properties); TEM (Technical or engineered material use); PREP
     (Preparation); USES (Uses)
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DERWENT-ACC-NO:

1999-018480

DERWENT-WEEK:

199944

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TITLE:

Liquid cyanic ester resin compostion - comprises cyanic ester resin, epoxy! resin, liquid at room temperature and

epoxy!-silicone oil, etc.

PATENT-ASSIGNEE: MITSUBISHI GAS CHEM CO INC[MITN]

PRIORITY-DATA: 1997JP-0096039 (April 14, 1997)

PATENT-FAMILY:

 PUB-NO
 PUB-DATE
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 JP 10287809 A
 October 27, 1998
 N/A
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APPLICATION-DATA:

PUB-NO APPL-DESCRIPTOR APPL-NO APPL-DATE

JP 10287809A N/A 1997JP-0096039 April 14, 1997

INT-CL (IPC): C08L063/00, C08L079/00, C08L083/06, H01L023/29,

H01L023/31

ABSTRACTED-PUB-NO: JP 10287809A

BASIC-ABSTRACT:

The compsn. comprises 100 pts.wt. of the compsn. of 25-60 pts.wt. of cyanic ester resin, 35-70 pts.wt. of epoxy resin, liquid at room temp., and 0.1-5 pts.wt. of epoxy-silicone oil, premixed with cyanic ester resin, 0.1-5 pts.wt. of the hardening catalyst of metal chelate or salt and 100-900 pts.wt. of fillers.

Also claimed is the semiconductor equipment sealed with the claimed compsn..

USE - The sealing material of electronic parts and semiconductor elements.

ADVANTAGE - The compsn. shows the high glass transition temp. (Tg) and the improved adhesion, electric properties and moisture resistance and the good heat resistance on soldering and gives the highly reliable semiconductor equipment with the less warpage.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: LIQUID CYANIC ESTER RESIN COMPOST COMPRISE CYANIC ESTER RESIN POLYEPOXIDE RESIN LIQUID ROOM TEMPERATURE POLYEPOXIDE SILICONE OIL

DERWENT-CLASS: A28 A85 L03 U11

CPI-CODES: A05-A01E2; A05-J02; A07-A03B; A08-D05; A10-E06; A12-E04; A12-E07C;

L04-C20A;

EPI-CODES: U11-A07; U11-E02A1;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1669U; 1694U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P1547 P1536 D01 D23 D22 D45 F19 F34 ; H0259 ; S9999 S1376

; S9999 S1434

Polymer Index [1.2]

018 ; G1570*R G1558 D01 D11 D10 D23 D22 D31 D42 D50 D69 D73 D83

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- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the semiconductor device using the liquefied closure resin constituent and this constituent which close a semiconductor device in PGA (pin grid array), BGA (ball grid array), MCM (multi chip module), or FC (flip chip).
[0002]

[Description of the Prior Art] According to the application and the purpose, an epoxy resin, silicone resin, polybutadiene, polyurethane, phenol resin, etc. are used for the resin seal of electronic parts and a semiconductor device. The epoxy resin is most broadly used among these from points, such as a mechanical characteristic, an electrical property, thermal resistance, an adhesive property, and chemical resistance. Especially, an epoxy resin is made to the semiconductor device closure with a molding compound, and it is used for it so much.

[0003] With the orientation to thin-shape-izing and the miniaturization of electronic parts in recently. increase of a degree of integration, etc., the configuration of a semiconductor device is diversified and it has become difficult to deal with the semiconductor device of all gestalten by the conventional epoxy resin molding compound. It is the semiconductor device integrated especially highly, and when bonding wire spacing must be narrowed, a bonding wire bends with the pressure of an inflow of the resin at the time of shaping, and it can become what contacts the next bonding wire. Liquefied resin is advantageous at the room temperature which a pressure with a bonding wire impossible for does not require for such the latest miniaturization and the semiconductor device integrated highly at the time of a resin seal. [0004] In order to raise the dependability of the package of BGA or MCM, it is indispensable that the adhesion of a closure ingredient, and a semiconductor device and a substrate resist is high. However, since a molding compound needs a release agent in order to fabricate it with metal mold, there is a limitation in improvement in the adhesion. Since the liquefied closure resin which does not use metal mold for shaping does not use a release agent as an indispensable component, the adhesion which was far excellent as compared with the molding compound is acquired, and its dependability of the can also improve. Moreover, in the case of the semiconductor device which connects a semiconductor device with an external electrode not with a bonding wire but with a solder ball, it is 20-200 of a semiconductor device and a packaging substrate. The resin seal of the gap of mum will be carried out using capillarity, and operation is difficult if it is not liquefied resin at a room temperature.

[0005] The liquefied epoxy resin constituent is proposed as liquefied closure resin to these requests. However, when liquefied closure resin is an epoxy resin constituent, the amine system compound, the acid anhydride, or the phenol system compound is made indispensable as a curing agent. Therefore, these epoxy liquefied closure resin is an inadequate property in thermal resistance or moisture resistance. Therefore, it is a problem that dependability with the sufficient semi-conductor sealing arrangement is not acquired, and improvement in the dependability of liquefied encapsulant is desired strongly.

[0006] Furthermore, the quality of the material which fixes a semiconductor device is cheap from a

leadframe or a ceramic, and is expanded to the easy organic substrate of processing. Liquefied closure resin which especially a thin organic substrate tends to generate curvature in the case of a resin seal, and is not made to generate the curvature is desired.

[0007]

[Problem(s) to be Solved by the Invention] The place which this invention was made in view of the above-mentioned fact, and is made into that purpose is to offer the semi-conductor sealing arrangement which closed the semiconductor device with the hardened material of the cyanic-acid ester liquefied resin constituent excellent in adhesion, thermal resistance, moisture resistance, an electrical property, etc., and this cyanic-acid ester liquefied resin constituent.

[Means for Solving the Problem] As a result of examining the liquefied resin constituent for the semiconductor device closures by polyfunctional cyanic-acid ester and the epoxy compound, this invention as an epoxy resin A liquefied epoxy resin or epoxy resin mixture is chosen at a room temperature. No epoxy curing agent or hardening accelerators, such as usual amine system resin or a compound, an acid anhydride, and phenol system resin, are used. When the epoxy group content silicone oil and epoxy resin which carried out preliminary mixing are made to react to polyfunctional cyanic-acid ester and cyanic-acid ester resin by the specific curing catalyst and it is made to harden, thermal resistance required for the resin for the semiconductor device closures, Even if it performed the closure to that what is excellent in moisture resistance and the adhesion force is obtained, and a thin fiber strengthening resin substrate, curvature found out the fully small thing, and this invention was further completed for examination in piles about this.

[0009] That is, this invention is (A). cyanic-acid ester resin. 25 - 60 weight section, (B) Epoxy resin liquefied at . room temperature Epoxy group content silicone oil which carried out preliminary mixing at 35 - 70 weight section and (C). cyanic-acid ester resin 0.1-5 Resin constituent which consists of the weight section In the 100 weight sections (D) Curing catalyst which consists of a . metal chelate or a metal salt 0.1 - 5 weight section and (E). bulking agent 200-900 The cyanic-acid ester liquefied resin constituent which comes to mix the weight section, It is the semiconductor device characterized by using this cyanic-acid ester liquefied resin constituent for a list, and coming to carry out the closure. [0010] Hereafter, each component which constitutes the constituent of this invention is explained to a detail. First, this invention constituent The polyfunctional cyanic-acid ester monomer used for the (A) component is a cyanate group shown in JP,41-1928,B. (-O-C**N) It is the compound which it has, and it is used, without being limited especially. Specifically, 2 and 2-screw (4-SHIANATO phenyl) propane, screw (4-SHIANATO -3, 5-dimethylphenyl) methane, screw (4-SHIANATO phenyl) thioether, 2, and 2-screw (4-SHIANATO phenyl) hexa FURORO propane and screw (4-SHIANATO phenyl) ethane are illustrated as a suitable thing.

[0011] moreover The cyanate of the phenol dicyclopentadiene copolymerization object shown in phenol novolak cyanate or JP,6-55814,B as made the resin and halogenation cyanogen which usually contain three or more phenolic hydroxyl groups react as a polyfunctional cyanic-acid ester compound used for the (A) component, and there is a compound which becomes considering this phenolic hydroxyl group as a cyanate group, for example, shown in JP,53-42076,B is mentioned. Further, The above-mentioned polyfunctional cyanic-acid ester monomer carries out the preliminary reaction of the (A) component, and it can be suitably used as a prepolymer. Extent of the polymerization of this prepolymer With 100-degree-C viscosity 0.1-1.0 A poise is desirable.

[0012] (B) As a liquefied epoxy resin of a component, at a room temperature, as long as it is liquefied, it may be good, and it may be single, or you may be the mixture of two or more kinds of epoxy resins. As a concrete epoxy resin, the diglycidyl ether of 2 and 2-screw (4-hydroxyphenyl) propane, 2 organic-functions epoxy compounds, such as diglycidyl ether of butadiene diepoxide, vinylcyclohexene dioxide, and resorcinol, The glycidyl ether which is made to carry out condensation of a polyhydric phenol or polyhydric alcohol, and the epichlorohydrin, and is obtained, Poly glycidyl ester, the novolak epoxy resin which is made to carry out condensation of novolak mold phenol resin and the epichlorohydrin, and is obtained, The epoxidation polyolefine and epoxidation polybutadiene which carried out

epoxidation by the peroxidating method are illustrated, and it uses as a preliminary reaction and two or more sort mixture suitably so that it may become liquefied at a room temperature.

[0013] In addition, a mono-epoxy compound can be suitably used together and styrene oxide, cyclohexene oxide, propylene oxide, methyl glycidyl ether, ethyl glycidyl ether, phenyl glycidyl ether, allyl glycidyl ether, octylene oxide, dodecen oxide, etc. are illustrated as this mono-epoxy compound. [0014] (C) The epoxy group content silicone oil in the epoxy group content silicone oil which carried out preliminary mixing at the cyanic-acid ester resin of a component is the following general formula (1). It is expressed.

General formula (1) R1Si(R)2-O-(SiRR2-O) n-Si: (R) Two R1 (among a formula) n 1-300 it is an integer -- R -- a methyl group or a phenyl group -- being shown -- R1 and R2 The organic radical which has a methyl group, a phenyl group, or an epoxy group is expressed, and the organic radical on which 1-10 of R1 or R2 pieces have an epoxy group is shown. [0015] Even when an epoxy group content silicone oil is independent, it is usable also as mixture, and the loadings are this invention. (A), (B), and (C) The sum total of a component Inside of the 100 weight sections 0.1-5 It uses in the amount used as the weight section. In adjustment of the constituent of this invention, it is this epoxy group content silicone oil. Preliminary mixing is beforehand carried out with a part or all of the (A) component, or it and a thing of the same kind, and it uses. When carrying out coincidence mixing of all the components of this invention and it adds, bleeding of a part of silicone oil is carried out, and properties, such as adhesive strength of the obtained constituent, fall. Preliminary mixing is because this epoxy group content silicone oil of 30 or less % of the weight of an amount is added to the cyanic-acid ester resin which carried out melting and it mixes to it. Phase separation is easy to happen and is not desirable if an addition exceeds 30 % of the weight. In the case of 2 and 2-screw (4-SHIANATO phenyl) propane, concrete mixed conditions are temperature. Stirring mixing is carried out in 140 - 180 ** for 4 to 18 hours.

[0016] (D) Use a metal chelate or a metal salt as a curing catalyst as a component. It is well-known for a metal chelate to be shown in JP,49-16800,B as the manufacture approach of the poly SHIANU rate, and to become the catalyst of independent hardening of cyanic-acid ester. Moreover, it is well-known in JP,61-501094,B that the metal salt of a carboxylic acid becomes the catalyst of independent hardening of cyanic-acid ester. Those all serve as cyanic-acid ester of this invention, and a catalyst excellent in epoxy hardening.

[0017] It is the metal chelate of the non-ion mold which generally has 1-6, or a chelate ring beyond it as a metal chelate, or an ion mold, and, specifically, iron, cobalt, zinc, tin, copper, manganese, a zirconium, titanium, vanadium, aluminum, and magnesium are desirable as a metal. Although it is known for the technical field concerned as a ligand of a metal chelate and there is especially no constraint well, the easy acetylacetone of acquisition, salichlaldehyde, a benzoylacetone, etc. are good. The metal as a metal salt catalyst of a carboxylic acid has iron, cobalt, zinc, tin, copper, manganese, a zirconium, titanium, vanadium, aluminum, and good magnesium, and a naphthenic acid or its octylic acid is good as a carboxylic acid.

[0018] what is examined and determined from LIFE of sufficient storage, and both sides of a required cure rate although the amount used as a catalyst changes with classes of catalyst -- it is -- usually -- (A) and (B) And (C) The sum total of a component the 100 weight sections -- carrying out -- 0.1 - 5 weight section -- it is -- desirable -- It is 0.3 - 3 weight section.

[0019] (E) The bulking agent as a component is made well-known in this kind of constituent, and it is easy to be usable [the bulking agent / the shape of fines of minerals or the quality of organic, a fibrous object etc.] to this. For example, although inorganic powder, such as composition or natural silica powder, fused-quartz powder, a mica, an alumina, a BOKI side, titanium oxide, a calcium carbonate, an antimony trioxide, silicon nitride, silicon carbide, a boron nitride, sulfuric-acid BARIUMU, clay, talc, carbon black, and graphite, synthetic-resin powder, river sand, slate powder, a glass fiber, rock wool, a synthetic fiber, etc. are mentioned, these may be one sort or two sorts or more of concomitant use. However, it dries beforehand in use and this bulking agent is that moisture content. What is considered as 0.3% or less is good, and in order to make good adhesion with the resinous principle which is a major

component of this invention, it is good to use together with a silane coupling agent or other processing aid. In addition, the loadings of this bulking agent are (A) and (B), although it changes with that class and viscosity. And (C) The sum total of a component As opposed to the 100 weight sections 100-900 It considers as the weight section.

[0020] It is also good to carry out initial-complement addition of a coloring agent, a defoaming agent, a leveling agent, the surfactant, etc. at the liquefied resin constituent of this invention, and to prepare an appearance and a configuration. The liquefied resin constituent of this invention is obtained by kneading each component to need to homogeneity using mixed equipments, such as a RAIKAI machine, a roll, and a kneader. There is especially no limit in the concrete approaches, such as the mixed sequence foreword.

[0021]

[Example] Next, this invention is not limited by these examples although this invention is explained based on an example and the example of a comparison. In addition, the "sections", such as an example, and "%" of especially publication is a weight standard unless it refuses.

an example 12 and 2-screw (4-SHIANETO phenyl) (name-of-article: -- BY 16-855 and the product made from Toray Industries Dow Corning Silicon --) Propane The 1,890 sections and epoxy group content silicone oil Weight per epoxy equivalent 650 General formula (1) It sets. R1 Glycidyl group, That by which R and R2 are equivalent to a methyl group The 210 sections At 170 degrees C Stirring mixing is carried out for 9 hours, and it is the preliminary mixing article of epoxy group content silicone oil 10% content. (it is described as "the preliminary mixing article C1" below) It obtained.

[0022] Cyanic-acid ester prepolymer (viscosity of 0.10poise, 100 degrees C) The 15 sections, bisphenol female mold epoxy resin (it LVP(s) trade name: -- EPICLON 830 --) the 55 made from Dainippon Ink Chemistry section, and neopentyl glycol diglycidyl ether Resin constituent (A:B:C=28.5:70:1.5) which consists of the 15 sections and the preliminary mixing article C115 section It is iron <3> acetylacetonate (Nihon Kagaku Sangyo Co., Ltd. make) as a curing catalyst. The 1.0 sections, It is gammaglycidoxypropyltrimetoxysilane as a coupling agent. (name of article: A-187, Nippon Unicar make) The two sections, Spherical silica of 10 micrometers of mean diameters (mix with an Ishikawa style raffle RAIKAI machine for 1 hour, and degassing of the MA-100 (Mitsubishi Chemical make) 0.5 section is carried out name of article:) It is carbon black as the 400 sections and a coloring agent. Cyanic-acid ester liquefied resin constituent (it is described as "Constituent A" below) It obtained.

[0023] An example 22 and 2-screw (4-SHIANETO phenyl) Propane The ten sections, The EPICLON

830 LVP 45 section, cyclohexane dimethanol diglycidyl ether (trade name: RIKAREJIN DME-100, product made from New Japan Chemical) The 20 sections and preliminary mixing article C1 Resin constituent (A:B:C=32.9:65:2.5) which consists of the 25 sections It is acetylacetone aluminum (Nihon Kagaku Sangyo Co., Ltd. make) as a curing catalyst. The 1.5 sections, The A-187 2 section, spherical silica with a mean particle diameter of 10 micrometers The 450 sections and MA-100 0.5 With an Ishikawa style raffle RAIKAI machine, it mixes for 1 hour, degassing of the section is carried out, and it is a cyanic-acid ester liquefied resin constituent. (it is described as "Constituent B" below) It obtained. [0024] An example 32 and 2-screw (4-SHIANETO phenyl) Propane The 17 sections, The EPICLON 830 LVP 45 section, neopentyl glycol diglycidyl ether The 12 sections, epoxidation polybutadiene (name of article: E1000-3.5, product made from Nippon Oil Chemistry) The three sections and preliminary mixing article C1 Resin constituent (A:B:C=39.5:60:2.5) which consists of the 25 sections It is octylic acid zinc as a curing catalyst. The 2.0 sections, A-187 The one section, spherical silica with a mean particle diameter of 10 micrometers The 450 sections and MA-100 0.5 With an Ishikawa style raffle RAIKAI machine, mix for 1 hour and degassing of the section is carried out. Cyanic-acid ester liquefied resin constituent (it is described as "Constituent C" below) It obtained.

[0025] an example 42 and 2-screw (4-SHIANETO phenyl) (name-of-article: -- SF 8411 and the product made from Toray Industries Dow Corning Silicon --) Propane The 1,700 sections and epoxy group content silicone oil Weight per epoxy equivalent 3,000 General formula (1) It sets and is in R2. 1-10 pieces Glycidyl group, That by which R and R1 are equivalent to a methyl group The 300 sections At 160 degrees C Stirring mixing is carried out for 9 hours, and it is an epoxy group content silicone oil.

Preliminary mixing article of 15% content (it is described as "the preliminary mixing article C2" below) It obtained. 2 and 2-screw (4-SHIANETO phenyl) Propane The 20 sections, the EPICLON 830 LVP 45 section, RIKAREJIN DME-100 The ten sections and preliminary mixing article C2 Resin constituent (A:B:C=41.25:55:3.75) which consists of the 25 sections Octylic acid zinc The 1.5 sections, A-187 The one section, spherical silica with a mean particle diameter of 10 micrometers The 400 sections and MA-100 0.5 With an Ishikawa style raffle RAIKAI machine, it mixes for 1 hour, degassing of the section is carried out, and it is a cyanic-acid ester liquefied resin constituent. (it is described as "Constituent D" below) It obtained.

[0026] Example of comparison 1EPICLON 830 LVP It is methyl cyclohexene-dicarboxylic anhydride as a curing agent of the 39 sections and an epoxy resin. The 47 sections, RIKAREJIN DME-100 The 11 sections, E1000-3.5 The three sections, It is 2-ethyl-4-methylimidazole as a hardening accelerator. The 0.5 sections, A-187 The two sections, spherical silica with a mean particle diameter of 10 micrometers The 450 sections and MA-100 0.5 With an Ishikawa style raffle RAIKAI machine, it mixes for 1 hour, degassing of the section is carried out, and it is a cyanic-acid ester liquefied resin constituent. (it is described as "Constituent E" below) It obtained.

[0027] the constituent obtained in the example and the example of a comparison -- using -- 1mm in thickness, and width of face 5mm 25mm angle with a frame the silicon chip with which the board of glass fabric base material copper clad laminate CCL-HL830 (product made from Mitsubishi Gas Chemical) of 0.4mm thickness was equipped is closed -- heat for 3 hours, and it was made to harden by 160 ** after 3-hour heating at 110 degree C, and considered as the test piece. The test result was shown in Table 1. The remarkable effectiveness of this invention was accepted.

[Table 1]

A trial item A unit Fruit ** Example example of a comparison etc. -- 1 2 3 4 1 A constituent name A sign A B C D E Viscosity A poise 900 850 800 900 650 Glass-transition-temperature ** 168 170 170 172 158 Bending strength kg/mm2 13 14 15 15 14 A volume resistivity x1010ohm cm9 88 9 0.2 Adhesion kg/cm 0.30 0.30 0.350.27 Amount of 0.10 curvatures mum 110 100 110 110120 Water absorption % 0.87 0.89 0.82 0.82 0.95 Solder thermal resistance 0/30 0/30 0/30 0/30 18/30 [0029] Measurement of various engine performance was performed by [as being the following].

- Viscosity: Unit The viscosity of 25 degrees C of a poise and the obtained liquefied resin constituent is measured using a Brookfield viscometer.
- glass transition point: Unit ** casting of the obtained liquefied resin constituent is carried out to metal mold -- it was made to harden at the 3:00 heating back and 160 degree C by 110 degree C for 3 hours, the 2x6x50mm test piece was created, and it measured using the apparatus for thermomechanical analysis.
- Bending strength: Unit kg/mm2 and the same test piece as the case of glass transition temperature are made, and it measures using an autograph.
- Moisture absorption: Unit % and the same test piece as the case of glass transition temperature are made, and it is this test piece. 121 degrees C, two atmospheric pressures, relative humidity It processed on 100% of PCT conditions for 24 hours, and considered as moisture absorption in quest of the weight rate of increase after processing.
- [0030] The amount of curvatures: Unit The curvature on the diagonal line of the opposite field which closed the closure and the above-mentioned test piece heated and obtained was measured using the surface roughness measurement machine using mum and a liquefied resin constituent.
- adhesion: Unit the 5cmx10cm liquefied resin constituent which flowed, pasted up the stop frame and was obtained within the limit is poured into the glossy surface side of the electrolytic copper foil of kg/cm and 35-micrometer thickness -- it was made to harden at the 3:00 heating back and 160 degree C by 110 degree C for 3 hours, and the test piece was created, and the with a width of face of 10mm glossy surface side of electrolytic copper foil lengthened, it removed, and reinforcement was measured using the autograph.

[0031] - solder thermal resistance: a liquefied resin constituent -- using -- the closure and the above-

mentioned test piece heated and obtained -- respectively -- It was immersed in the solder bath of 240 degree C after using 30 pieces at a time and carrying out moisture absorption processing of 85 degrees C, 85%, and 24 hours for 1 minute. Then, the package front face and the cross section were observed with the stereoscopic microscope, and the number of defects / the number of trials showed the result of having evaluated the existence of generating of an external resin crack and an internal crack, or the existence of exfoliation.

- volume resistivity: Unit casting of omegacm and the obtained liquefied resin constituent is carried out to metal mold -- it hardens at the 3:00 heating back and 160 degree C by 110 degree C for 3 hours -- making -- a test piece with a 2mm diameter [in thickness] of 90mm -- creating -- this test piece 121 degrees C, two atmospheric pressures, and relative humidity It processed on 100% of PCT conditions for 24 hours, and measured using the insulating measuring device after processing. [0032]

[Effect of the Invention] The amount of curvatures of the semi-conductor sealing arrangement which the cyanic-acid ester liquefied resin constituent of this invention showed a high glass transition temperature, was excellent in adhesion, an electrical property, moisture resistance, and solder thermal resistance, and used the cyanic-acid ester liquefied resin constituent of this invention is also small, and its dependability is highly useful so that clearly from a detailed description and the following, an example, the example of a comparison, and Table 1.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] (A) . cyanic-acid ester resin Epoxy resin liquefied at 25 - 60 weight section and (B). room temperature Epoxy group content silicone oil which carried out preliminary mixing at 35 - 70 weight section and (C). cyanic-acid ester resin Resin constituent which consists of the 0.1 - 5 weight section In the 100 weight sections (D) Curing catalyst which consists of a metal chelate or a metal salt 0.1 - 5 weight section and (E). bulking agent 100-900 Cyanic-acid ester liquefied resin constituent which comes to mix the weight section.

[Claim 2] The semiconductor device characterized by coming to carry out the closure using a cyanic-acid ester liquefied resin constituent according to claim 1.

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(21)出顧番号		特顧平9 -96039	(71)出顧人	000004466 三菱瓦斯化学株式会社				
(00) ([1886])		W-P-0-10070 A H14 H				отнежов		
(22)出顧日		平成9年(1997)4月14日	東京都千代田区丸の内2丁目5番2 (72)発明者 本折 進					
						11番1号 三菱瓦		
			j		林式会社東京工 地			
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(54) 【発明の名称】 シアン酸エステル液状樹脂組成物及び半導体封止装置

(57)【要約】

【課題】 信頼性の高い封止した半導体素子を得る。

【解決手段】 (A).シアン酸エステル樹脂 25~60重量 部、(B).室温で液状であるエポキシ樹脂 35~70重量部 および(C).シアン酸エステル樹脂に予備混合したエポキシ基含有シリコンオイル 0.1~5重量部からなる樹脂組成物 100重量部に、(D).金属キレート又は金属塩からなる硬化触媒 0.1~5重量部および(E).充填剤 100~900重量部を混合してなるシアン酸エステル液状樹脂組成物、および該シアン酸エステル液状樹脂組成物、および該シアン酸エステル液状樹脂組成物を用いて封止されてなることを特徴とする半導体装置。

【効果】 密着性、電気特性に優れ、ボイドの発生やチップの反りが小さく、半田後の耐湿信頼性等の特性に著しく優れた半導体素子を封止した半導体封止装置が提供できる。

【特許請求の範囲】

【請求項1】 (A).シアン酸エステル樹脂 25~60重量部、(B).室温で液状であるエポキシ樹脂 35~70重量部および(C).シアン酸エステル樹脂に予備混合したエポキシ基含有シリコンオイル 0.1~5重量部からなる樹脂組成物 100重量部に、(D).金属キレート又は金属塩からなる硬化触媒 0.1~5重量部および(E).充填剤 100~900重量部を混合してなるシアン酸エステル液状樹脂組成物。

【請求項2】 請求項1に記載のシアン酸エステル液状 10 樹脂組成物を用いて封止されてなることを特徴とする半 導体装置。

【発明の詳細な説明】

[0001]

【産業上の利用分野】本発明はPGA(ピングリッドアレイ)、BGA(ボールグリッドアレイ)、MCM(マルチチップモジュール)やFC(フリップチップ)において半導体素子を封止する液状封止樹脂組成物及び該組成物を用いた半導体装置に関する。

[0002]

【従来の技術】電子部品、半導体素子の樹脂封止には、その用途、目的に応じてエポキシ樹脂、シリコーン樹脂、ポリブタジエン、ポリウレタン、フェノール樹脂などが用いられている。これらのうちで、機械特性、電気特性、耐熱性、接着性及び耐薬品性などの点からエポキシ樹脂が最も広範囲に使用されている。特に、半導体素子封止にはエポキシ樹脂をモールディングコンパウンドとなして多量に使用されている。

【0003】最近における電子部品の薄型化や小型化への指向、集積度の増大などに伴って、半導体装置の形状 30 は多様化しており、従来のエボキシ樹脂モールディングコンパウンドで全ての形態の半導体装置に対応することは困難となってきた。特に、高集積化した半導体素子であって、ボンディングワイヤ間隔を狭くせざるをえない場合、成形時の樹脂の流入の圧力によりボンディングワイヤが曲がり、隣のボンディングワイヤと接触するようなことにもなり得る。このような最近の小型化、高集積化された半導体装置には、樹脂封止時にボンディングワイヤに無理な圧力のかからない室温で液状の樹脂が有利になっている。 40

【0004】BGAやMCMのパッケージの信頼性を向上させるには、封止材料と半導体素子や基板レジストとの密着性が高いことが必須である。しかし、モールディングコンパウンドは金型により成形するため、離型剤を必要とするため、その密着性の向上には限界がある。成形に金型を使用しない液状封止樹脂は、離型剤を必須の成分としないので、モールディングコンパウンドに比較してはるかに優れた密着性が得られ、その信頼性も向上できる。また、半導体素子をボンディングワイヤではなく半田ボールで外部電極と接続する半導体装置の場合

は、半導体素子とパッケージング基板の20~200 µmの 間隙を毛管現象を利用して樹脂封止することとなり、室 温で液状の樹脂でなければ実施は困難である。

【0005】これらの要望に対する液状対止樹脂として液状エボキシ樹脂組成物が提案されている。しかし、液状対止樹脂がエボキシ樹脂組成物の場合、アミン系化合物、酸無水物或いはフェノール系化合物等を硬化剤として必須としている。そのために、それらエボキシ液状対止樹脂は、耐熱性あるいは耐湿性において不十分な特性である。そのため、その半導体封止装置は充分な信頼性が得られないことが問題であり、液状対止剤の信頼性の向上が強く望まれている。

【0006】さらには、半導体素子を固定する材質はリードフレームやセラミックから安価で加工の容易な有機 基板へと拡大している。特に薄い有機基板は樹脂封止の 際に反りを発生し易く、その反りを発生させない液状封 止樹脂が望まれている。

[0007]

【発明が解決しようとする課題】本発明は上述の事実に 20 鑑みてなされたもので、その目的とするところは、密着 性、耐熱性、耐湿性及び電気特性等に優れたシアン酸エ ステル液状樹脂組成物、及びこのシアン酸エステル液状 樹脂組成物の硬化物によって、半導体素子を封止した半 導体封止装置を提供することにある。

[0008]

【課題を解決するための手段】本発明は、多官能シアン酸エステルとエボキシ化合物による半導体素子封止用の液状樹脂組成物について検討した結果、エボキシ樹脂として、室温で液状であるエボキシ樹脂またはエボキシ樹脂混合物を選択し、通常のアミン系樹脂または化合物、酸無水物、フェノール系樹脂等のエボキシ硬化剤或いは硬化促進剤を一切使用せず、多官能シアン酸エステル、シアン酸エステル樹脂に予備混合したエボキシ基含有シリコンオイルおよびエボキシ樹脂を特定の硬化触媒により反応させて硬化させると半導体素子封止用樹脂に必要な耐熱性、耐湿性、密着力に優れるものが得られること、および薄い繊維強化樹脂基板に封止を行っても反りが充分に小さいことを見いだして、これについてさらに検討を重ねて本発明を完成させた。

40 【0009】すなわち、本発明は、(A).シアン酸エステル樹脂 25~60重量部、(B).室温で液状であるエポキシ樹脂 35~70重量部および(C).シアン酸エステル樹脂に予備混合したエポキシ基含有シリコンオイル 0.1~5 重量部からなる樹脂組成物 100重量部に、(D).金属キレートまたは金属塩からなる硬化触媒 0.1~5重量部および(E).充填剤 200~900 重量部を混合してなるシアン酸エステル液状樹脂組成物、並びに該シアン酸エステル液状樹脂組成物を用いて封止されてなることを特徴とする半導体装置である。

50 【0010】以下、本発明の組成物を構成する各成分に

ついて詳細に説明する。まず、本発明組成物の(A)成分 に用いる多官能シアン酸エステルモノマーは特公昭41-1 928 号公報に示されているシアナト基 (-O-C≡N) を有する化合物であり、特に限定されることなく使用さ れる。具体的には、2,2-ビス(4-シアナトフェニル)プ ロパン、ビス(4ーシアナトー3,5-ジメチルフェニル) メ タン、ビス(4ーシアナトフェニル) チオエーテル、2,2-ビス(4-シアナトフェニル) ヘキサフロロプロパン及び ビス(4-シアナトフェニル) エタンが好適なものとして 例示される。

【0011】また、(A)成分に用いる多官能シアン酸工 ステル化合物としては、フェノール性水酸基を通常3個 以上含有する樹脂とハロゲン化シアンを反応させて、該 フェノール性水酸基をシアナト基としてなる化合物があ り、例えば、特公昭53-42076号公報に示される様なフェ ノールノボラックシアネートあるいは特公平6-55814号 公報に示されるフェノール・ジシクロペンタジエン共重 合物のシアネートが挙げられる。さらに、(A)成分は、 上記の多官能シアン酸エステルモノマーの予備反応させ てプレポリマーとして好適に使用できる。このプレポリ 20 マーの重合の程度は 100°C粘度で 0.1~1.0 ポイズが好 ましい。

【0012】(B) 成分の液状エポキシ樹脂としては、室 温で液状であればよく、単一でも、2種類以上のエポキ シ樹脂の混合物であってもよい。具体的なエポキシ樹脂 としては、2,2-ビス(4-ヒドロキシフェニル) プロパン のジグリシジルエーテル、ブタジエンジエポキシド、ビ ニルシクロヘキセンジオキシド、レゾルシンのジグリシ ジルエーテルなどの2官能エポキシ化合物、多価フェノ 合させて得られるグリシジルエーテル、ポリグリシジル エステル、ノボラック型フェノール樹脂とエピクロルヒ ドリンとを縮合させて得られるノボラックエポキシ樹 脂、過酸化法によりエポキシ化したエポキシ化ポリオレ フィン、エポキシ化ポリブタジエンが例示され、室温で 液状となるように適宜、予備反応、2種以上混合物とし て用いる。

【0013】なお、モノエポキシ化合物を適宜併用する ことができ、このモノエボキシ化合物としてはスチレン オキシド、シクロヘキセンオキシド、プロピレンオキシ 40 ド、メチルグリシジルエーテル、エチルグリシジルエー テル、フェニルグリシジルエーテル、アリルグリシジル エーテル、オクチレンオキシド、ドデセンオキシドなど が例示される。

【0014】(C) 成分のシアン酸エステル樹脂に予備混 合したエポキシ基含有シリコンオイルにおけるエポキシ 基含有シリコンオイルは、下記一般式(1) で表されるも のである。

一般式(1): R¹Si(R)₂-O-(SiRR²-O)_n-Si(R)₂R¹ (式中、n は 1~300 の整数であり、 Rはメチル基また

はフェニル基を示し、R1,R2 はメチル基、フェニル基ま たはエポキシ基を有する有機基を表し、R1またはR2のう ち、1~10個がエポキシ基を有する有機基を示す。) 【0015】エポキシ基含有シリコンオイルは単独でも 混合物としても使用可能であり、その配合量は、本発明 の (A), (B)および(C) 成分の合計 100重量部中の 0.1~ 5 重量部となる量で用いる。本発明の組成物の調整に は、本エポキシ基含有シリコンオイルを(A)成分の一部 或いは全部またはそれと同種のものと予め予備混合して 10 用いる。本発明の全成分を同時混合するときに、添加し た場合、シリコンオイルの一部はブリードし、また、得 られた組成物の接着力等の特性が低下する。予備混合 は、溶融させたシアン酸エステル樹脂に30重量%以下の 量の本エポキシ基含有シリコンオイルを添加し混合する ことによる。添加量が30重量%を越えると相分離が起こ りやすく好ましくない。具体的な混合条件は、例えば、 2,2-ビス(4-シアナトフェニル) プロパンの場合、温度 140~180 ℃において、4~18時間攪拌混合する。

【0016】(D) 成分として、金属キレート又は金属塩 を硬化触媒として用いる。金属キレートは特公昭49-168 00号公報にポリシアヌレートの製造方法として示され、 シアン酸エステルの単独硬化の触媒になることは公知で ある。また、カルボン酸の金属塩がシアン酸エステルの 単独硬化の触媒になることは特公昭61-501094 号公報に おいて公知である。それらのいずれも本発明のシアン酸 エステルとエポキシの硬化に優れた触媒となる。

【0017】具体的には、金属キレートとして一般に1 ~6またはそれ以上のキレート環を有する非イオン型ま たはイオン型の金属キレートであり、金属として鉄、コ ールまたは多価アルコールとエピクロルヒドリンとを縮 30 バルト、亜鉛、錫、銅、マンガン、ジルコニウム、チタ ニウム、バナジン、アルミニウムおよびマグネシウムが 好ましい。金属キレートの配位子としては当該技術分野 で知られているものでよく特に制約はないが、入手の容 易なアセチルアセトン、サリチルアルデヒド、ベンゾイ ルアセトン等がよい。カルボン酸の金属塩触媒としての 金属は、鉄、コバルト、亜鉛、錫、銅、マンガン、ジル コニウム、チタニウム、バナジン、アルミニウムおよび マグネシウムがよく、カルボン酸としてナフテン酸ある いはオクチル酸がよい。

> 【0018】触媒として使用する量は、触媒の種類によ り異なるが、充分な保管のライフと必要な硬化速度の両 面から検討し決定するもので、通常は(A),(B) および (C) 成分の合計を 100重量部として 0.1~5重量部であ り、好ましくは 0.3~3重量部である。 【0019】(E) 成分としての充填剤はこの種の組成物

に於いて公知とされているものでよく、これには無機質 または有機質の微粉状、繊維状物などが使用可能であ る。例えば合成または天然のシリカ粉末、溶融石英粉 末、マイカ、アルミナ、ボーキサイド、酸化チタン、炭 50 酸カルシウム、三酸化アンチモン、窒化珪素、炭化珪

素、窒化ほう素、硫酸バリゥム、クレー、タルク、カーボンブラック、グラファイトなどの無機粉末、合成樹脂粉末、川砂、スレート粉末、ガラス繊維、ロックウール、合成繊維などが挙げられるが、これらは1種または2種以上の併用であってもよい。しかし、この充填剤は使用に当たって予め乾燥してその水分量を0.3%以下としておくことがよく、また本発明の主要成分である樹脂成分との密着性を良好にするためシランカップリング剤またはその他の加工助剤と併用することがよい。なお、この充填剤の配合量はその種類、粘度により異なるが、(A)、(B) および(C) 成分の合計 100重量部に対して100~900 重量部とする。

【0020】本発明の液状樹脂組成物に着色剤、消泡 剤、レベリング剤、界面活性剤等を必要量添加し、外 観、形状を整えることもよい。本発明の液状樹脂組成物 は、必要とする各成分をライカイ機、ロール、ニーダー などの混合装置を用いて均一に混練することにより得ら れる。その混合順序等の具体的方法に特に制限はない。 【0021】

【実施例】次に本発明を実施例、比較例に基づいて説明 20 するが、本発明はこれらの実施例によって限定されるものではない。なお、実施例などの「部」、「%」の記載は特に断らない限り重量規準である。

実施例1

2,2-ビス(4-シアネトフェニル) プロパン 1,890部とエポキシ基含有シリコンオイル (品名: BY16-855、東レ・ダウコーニング・シリコン (株) 製、エボキシ当量 65 0、一般式(1) において、R1 がグリシジル基、R,R2 がメチル基に相当するもの) 210部とを 170℃で 9時間攪拌混合し、エボキシ基含有シリコンオイル10%含有の予備 30 混合品 (以下「予備混合品C1」と記す)を得た。

【0022】シアン酸エステルプレポリマー(粘度0.10 ポイズ,100℃) 15部、ビスフェノールF型エポキシ樹脂 (商品名:EPICLON 830 LVP、大日本インキ化学(株) 製) 55部、ネオペンチルグリコールジグリシジルエーテル 15部および予備混合品C115部からなる樹脂組成物 (A:B:C=28.5:70:1.5) に、硬化触媒としてアセチルアセトン鉄(日本化学産業(株)製) 1.0部、カップリング 剤としてァーグリシドキシプロピルトリメトキシシラン (品名:A-187、日本ユニカー(株)製) 2部、平均粒径 40 10μmの球状シリカ 400部および着色剤としてカーボンブラック(品名:MA-100(三菱化学(株)製) 0.5部を、石川式カクハンライカイ機で1時間混合し、脱泡して、シアン酸エステル液状樹脂組成物(以下「組成物 A」と記す)を得た。

【0023】実施例2

2,2-ビス(4-シアネトフェニル) プロパン 10部、EPIC LON 830 LVP 45部、シクロヘキサンジメタノールジグリシジルエーテル (商品名: リカレジン DME-100、新日本理化(株)製) 20部および予備混合品C1 25部からなる 50

樹脂組成物(A:B:C=32.9:65:2.5) に、硬化触媒としてアセチルアセトンアルミニウム (日本化学産業(株)製) 1.5部、A-187 2部、平均粒径10μmの球状シリカ 450部およびMA-100 0.5部を、石川式カクハンライカイ機で1時間混合し、脱泡して、シアン酸エステル液状樹脂組成物(以下「組成物B」と記す)を得た。

2,2-ビス(4-シアネトフェニル) プロパン 17部、EPIC LON 830 LVP 45部、ネオペンチルグリコールジグリシジ 10 ルエーテル 12部、エポキシ化ポリブタジエン(品名:E1 000-3.5、日本石油化学(株)製) 3部および予備混合品C1 25部からなる樹脂組成物(A:B:C=39.5:60:2.5) に、硬化触媒としてオクチル酸亜鉛 2.0部、A-187 1部、平均粒径10μmの球状シリカ 450部およびMA-100 0.5 部を、石川式カクハンライカイ機で1時間混合し、脱泡して、シアン酸エステル液状樹脂組成物(以下「組成物C」と記す)を得た。

【0025】実施例4

【0024】実施例3

2.2-ビス(4ーシアネトフェニル) プロバン 1,700部とエボキシ基含有シリコンオイル (品名:SF 8411、東レ・ダウコーニング・シリコン (株) 製、エボキシ当量 3,00 0、一般式(1) において、R²の中の 1~10個がグリシジル基、R,R¹がメチル基に相当するもの) 300部とを 160 でで 9時間攪拌混合し、エボキシ基含有シリコンオイル 15%含有の予備混合品 (以下「予備混合品(2」と記す)を得た。2.2-ビス(4ーシアネトフェニル) プロバン 20部、EPICLON 830 LVP 45部、リカレジン DME-100 10部および予備混合品(2 25部からなる樹脂組成物(A:B:C=41.25:55:3.75) に、オクチル酸亜鉛 1.5部、A-187 1部、平均粒径10μmの球状シリカ 400部およびMA-10 0 0.5 部を、石川式カクハンライカイ機で1時間混合し、脱泡して、シアン酸エステル液状樹脂組成物(以下「組成物D」と記す)を得た。

【0026】比較例1

EPICLON 830 LVP 39部、エポキシ樹脂の硬化剤としてメチルテトラヒドロ無水フタル酸 47部、リカレジン D ME-100 11部、E1000-3.5 3部、硬化促進剤として2-エチルー4-メチルイミダゾール 0.5部、A-187 2部、平均粒径10μmの球状シリカ 450部およびMA-100 0.5 部を、石川式カクハンライカイ機で1時間混合し、脱泡して、シアン酸エステル液状樹脂組成物(以下「組成物 E」と記す)を得た。

【0027】実施例及び比較例で得られた組成物を用いて、厚さ1 m、幅 5mmの枠付きの25mm角の 0.4mm厚みのガラス布基材銅張積層板CCL-HL830(三菱ガス化学(株)製)のボードに装着したシリコンチップを封止し、 110 ℃で3時間加熱後、160 ℃で3時間加熱して硬化させ、テストピースとした。試験結果を表1に示した。本発明の顕著な効果が認められた。

[0028]

【表1】

試験項目	単位	実 加	徳 例			比較例
など		1	2	3	4	1
組成物名称	符号	Α	В	С	D	E
粘度	ポイズ	900	850	800	900	650
ガラス転移温度	\mathcal{C}	168	170	170	172	158
曲げ強さ	kg/mm²	13	14	15	15 .	14
体積抵抗率	$ imes 10^{10}\Omega$ cm	9	8	8	9	0.2
密着性	kg/cm	0.30	0.30	0.35	0.27	0.10
反り量	μm	110	100	110	110	120
吸水率	%	0.87	0.89	0.82	0.82	0.95
半田耐熱性		0/30	0/30	0/30	0/30	18/30

【0029】各種性能の測定は以下のようにして行った。

- ・粘度 : 単位 ポイズ、得られた液状樹脂組成物の25 ℃の粘度をB型粘度計を用いて測定。
- ・ガラス転移点: 単位 ℃、 得られた液状樹脂組成物を金型に注型し、110℃で3時加熱後、160℃で3時間硬化させ、2×6×50mmの試験片を作成し、熱機械分析装置を用いて測定した。
- ・曲げ強さ: 単位 kg/m²、ガラス転移温度の場合と 同様な試験片を作り、オートグラフを用いて測定。
- ・吸湿率 : 単位 %、ガラス転移温度の場合と同様な試験片を作り、この試験片を 121℃、2気圧、相対湿度 100%のPCT条件で24時間処理し、処理後の重量増加率を求めて吸湿率とした。

【0030】・反り量 : 単位 μm、液状樹脂組成物を用いて、封止、加熱して得られた上記のテストピースを、封止した反対の面の対角線上の反りを表面粗さ測定機を用いて測定した。

・密着性 : 単位 kg/cm 、35μm厚みの電解網箔の 光沢面側に5cm×10cmの流れ止め枠を接着し、枠内に得 られた液状樹脂組成物を注入し、110°Cで3時加熱後、 160°Cで3時間硬化させて試験片を作成し、幅10mmの電* *解銅箔の光沢面側の引き剥し強度をオートグラフを用いて測定した。

【0031】・半田耐熱性 : 液状樹脂組成物を用いて、封止、加熱して得られた上記のテストピースをそれぞれ 30個づつ用いて、85℃、85%、24時間の吸湿処理をした後、240℃の半田浴に1分間浸漬した。その後、実体顕微鏡でパッケージ表面及びクロスセクションを観20 察し、外部樹脂クラックの発生の有無及び内部のクラックあるいは剥離の有無を評価した結果を不良数/試験数で示した。

・体積抵抗率 : 単位 Ωcm、得られた液状樹脂組成物を金型に注型し、110℃で3時加熱後、160℃で3時間硬化させ、厚さ2mm直径90mmの試験片を作成し、この試験片を121℃、2気圧、相対湿度100%のPCT条件で24時間処理し、処理後絶縁測定装置を用いて測定した。【0032】

【発明の効果】発明の詳細な説明及び下記、実施例、比 90 較例および表1から明らかなように、本発明のシアン酸 エステル液状樹脂組成物は高いガラス転移温度を示し、 密着性、電気特性、耐湿性、半田耐熱性に優れ、本発明 のシアン酸エステル液状樹脂組成物を使用した半導体封 止装置は反り量も小さく、信頼性が高く有用である。